

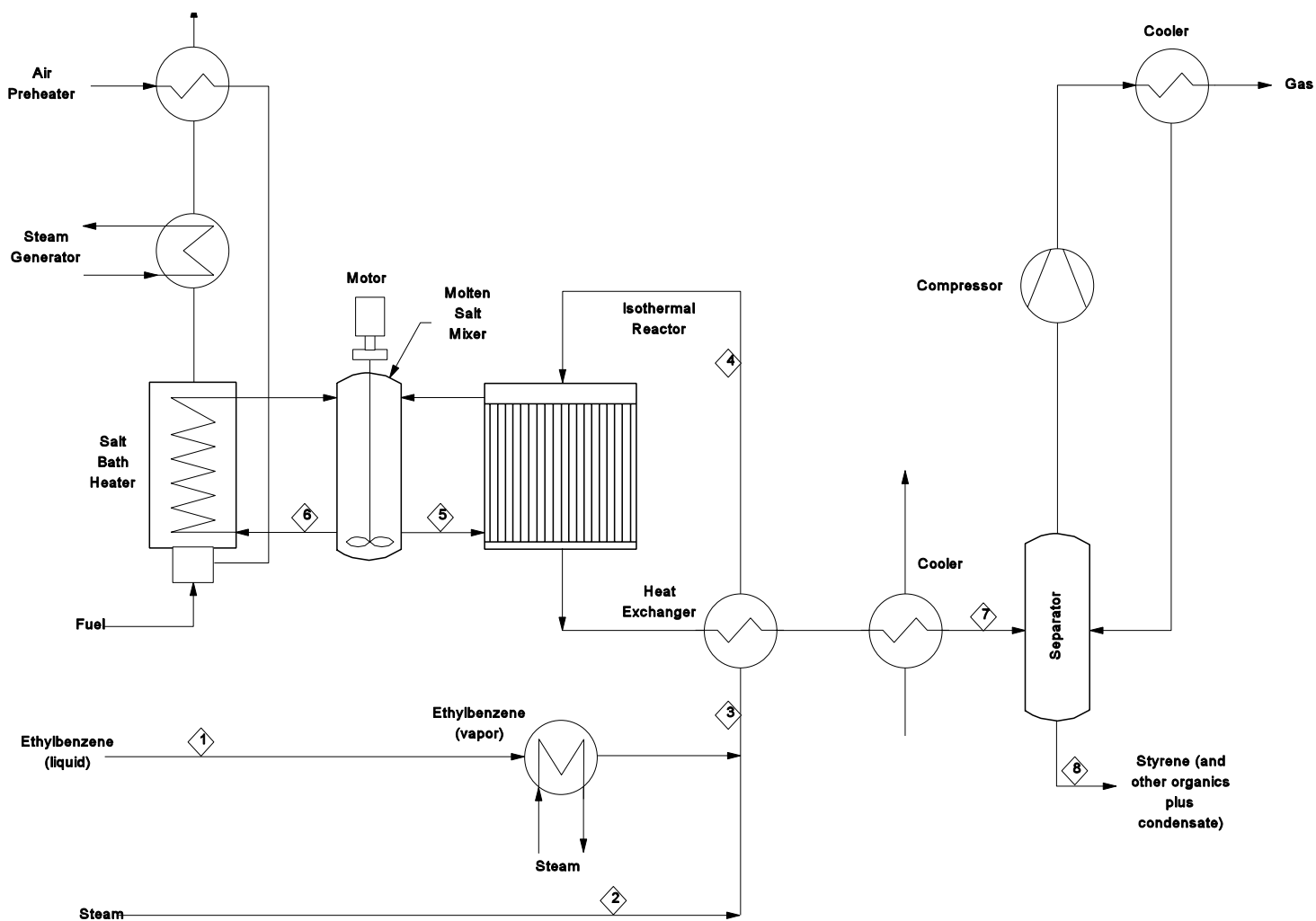
The mixed stream of α -methyl-benzyl alcohol and acetophenone (Stream 7) is then dehydrated over a solid catalyst to produce styrene. Residual catalyst solids and high-boiling impurities are separated and collected for disposal. The crude styrene goes to a series of distillation columns, where the pure styrene monomer product is recovered. The residual organic stream contains crude acetophenone, catalyst residue, and various impurities. This mixture is treated under pressure with hydrogen gas to convert the acetophenone to α -methyl-benzyl alcohol. Catalyst waste is separated from the α -methyl-benzyl alcohol, which is returned to the recovery section for processing and reuse. Hydrogen and organic vapors are recovered for use as fuel.

5.1.4 Process Description for Styrene Production by an Isothermal Process

Ethylbenzene may also be converted to styrene by an isothermal process (Figure 5-4). Liquid ethylbenzene is vaporized by condensing steam in a heat exchanger (Stream 1). Process steam (Stream 2) is then introduced into the ethylbenzene stream and the feed mixture is superheated (Stream 3) before it enters the molten-salt reactor (Stream 4) (see Figure 5-4).⁷⁵

In the reactor, the ethylbenzene/steam mixture passes through the tubes, where it comes into contact with the catalyst and is dehydrogenated. Heat for the dehydrogenation reaction is supplied by molten salt (preferably a mixture of sodium carbonate, lithium carbonate, and potassium carbonate) surrounding the tubes (Stream 5). The reactor is maintained at a uniform wall temperature by circulating the molten-salt mixture through the heat exchanger of a fired heater (Stream 6).⁷⁵

The reaction products are cooled and condensed in a separator (Stream 7). The liquid phase is a mixture of organic products: styrene, unreacted ethylbenzene, and small quantities of benzene, toluene, and high-boiling compounds. Styrene (Stream 8) is separated from the other liquid constituents, which then are recovered and recycled.⁷⁵



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 5-4. Isothermal Processing of Styrene

Source: Reference 75.

The gas phase from the condensation step in the separator consists mainly of hydrogen, with small quantities of CO₂, CO, and methane. After these gases are compressed, they are cooled. Condensable products from this final cooling stage are then recovered and recycled to the separator. When hydrogen-rich offgas is used as fuel for the heater of the molten-salt reactor, the fuel requirement for this stage of the process is zero.⁷⁵

5.1.5 Benzene Emissions from Ethylbenzene and Styrene Production via Alkylation and Dehydrogenation

Emission Estimates from Ethylbenzene Production and Dehydrogenation to Styrene

Emission factors have been developed based on an uncontrolled 300-million-kg/yr capacity integrated ethylbenzene/styrene production plant. Major process emission sources are the alkylation reactor area vents (Vent A in Figure 5-1), atmospheric and pressure column vents (Vents B, C, and D in Figure 5-1), vacuum column vents (Vent B in Figure 5-2), and the hydrogen separation vent (Stream 7 in Figure 5-2). Emission factors from these sources are given in Table 5-2.^{69,74} The first four process vent streams in Table 5-2 are low-flow, high-concentration streams. The hydrogen separation stream (Stream 7 in Figure 5-2) is high-flow, low-concentration. Other emission sources listed in Table 5-2 include storage losses and shipment losses (Vent G). Fugitive emissions from valves and other equipment leaks are not indicated in Figure 5-1 or 5-2.

Reactor area vents remove various inerts plus entrained aromatics (benzene). Inerts include nitrogen or methane used in pressure control, unreacted ethylene, reaction byproducts, and ethylene feed impurities. In typical plants using liquid-phase aluminum chloride catalyst with high-purity ethylene, vent streams are usually cooled and scrubbed to recover aromatics. In plants using the newer solid support catalysts of the UOP or Mobil/Badger process, reactor vent flow rates are very high because of the low-purity ethylene feed. Process economics requires that these vent gases be burned as fuel.

TABLE 5-2. EMISSION FACTORS FOR ETHYLBENZENE/STYRENE PRODUCTION VIA
ALKYLATION AND DEHYDROGENATION

SCC and Description	Emission Source	Control Device	Emission Factor in lb/ton (kg/Mg) ^a	Factor Rating
3-01-169-02 Ethylbenzene Manufacturing - Alkylation Reactor Vent	Alkylation Reactor Vent	Process Heater	0.0006 (0.0003)	U
		Uncontrolled	0.6 ^b (0.3)	U
3-01-169-03 Ethylbenzene Manufacturing - Benzene Drying Column	Atmospheric/Pressure Column Vents ^d	Flare	0.024 ^b - 0.96 ^d (0.012 - 0.48)	U
		Uncontrolled	2.4 ^b (1.2)	U
3-01-169-04 Ethylbenzene Manufacturing - Benzene Recovery Column				
3-01-169-05 Ethylbenzene Manufacturing - Ethylbenzene Recovery Column				
3-01-169-06 Ethylbenzene Manufacturing - Polyethylbenzene Recovery Column	Other Vacuum Vents ^e	Flare	0.0010 ^b - 0.004 ^d (0.005 - 0.002)	U
		Uncontrolled	0.10 ^b (0.05)	U
3-01-206-02 Styrene Manufacturing - Benzene Recycle Column				
3-01-206-03 Styrene Manufacturing - Styrene Purification Vents				
3-01-206-XX Styrene Manufacturing -Benzene - Toluene Vacuum Vent	Benzene-Toluene Vacuum Vent	Flare	0.06 ^b - 2.4 ^d (0.03 - 1.2)	U
		Uncontrolled	6.0 ^b (3.0)	U

(continued)

TABLE 5-2. CONTINUED

SCC and Description	Emission Source	Control Device	Emission Factor in lb/ton (kg/Mg) ^a	Factor Rating
3-01-206-XX Styrene Manufacturing - Hydrogen Separation Vent	Hydrogen Separation Vent	Flare	0.00006 ^b - 0.0024 ^d (0.00003 -0.0012)	U
		Uncontrolled	0.006 ^d (0.003)	U
3-01-169-80/3-01-206-80 Ethylbenzene/Styrene Manufacturing - Equipment Leaks	Equipment Leaks	Detection and Correction Uncontrolled	See Section 4.5.2	
4-07-196-XX/4-07-196-13 Ethylbenzene/Styrene Manufacturing - Storage and Handling	Storage and Handling	Floating Roof, Vented to Flare, Refrigerated Vent Condenser, and Uncontrolled	See Section 4.5.3	

^a Emission factors are for a model plant with capacity 661 million lbs (300 million kg) per year. Actual emission factors may vary with throughput and control measures and should be determined through direct contacts with plant personnel. Factors are expressed as lb (kg) benzene emitted per ton (Mg) ethylbenzene/styrene produced.⁶⁹

^b Reference 74.

^c Includes the following vents: benzene drying column, benzene recovery column, and ethylbenzene recovery column.

^d Reference 69.

^e Includes the following vents: polyethylbenzene recovery column at ethylbenzene plants; and benzene recycle column and styrene purification vents at styrene plants.

Atmospheric and column vents remove non-combustibles in the column feeds, light aliphatic hydrocarbons, and any entrained aromatics. The benzene drying column also removes impurities in the benzene feed. Most emissions occur in the first column of the distillation train (benzene recovery column in Figure 5-1).

Vacuum column vents remove air that leaks into the column, light hydrocarbons and hydrogen formed in dehydrogenation, non-combustibles in the column feed, and entrained aromatics. Most emissions occur on the benzene/toluene column (vent A in Figure 5-2). Uncontrolled distillation vents emit 4.2×10^{-3} lb hydrocarbons/lb styrene (4.2×10^{-3} kg hydrocarbons/kg styrene) in one plant where the hydrocarbons are benzene and toluene. Another condenser controlled vent emits 0.4×10^{-3} lb benzene/lb styrene (0.4×10^{-3} kg benzene/kg styrene).⁹

Following dehydrogenation, a hydrogen-rich gas (Stream 4 in Figure 5-2) containing methane, ethane, ethylene, CO₂, CO, and aromatics is normally cooled and compressed to recover aromatics. The stream should be vented to the atmosphere (Vent E in Figure 5-2) only during startup, shutdown, and recovery section compressor outages. Some plants may also vent this stream to a flare. Flares are an efficient (99 percent) emission control only when flare diameter and gas flow are closely matched for optimum turbulence and mixing. Emissions can be better controlled when the stream is routed to a manifold and burned with other fuels.

Stripper vents have been reported to emit 0.032 lb ethylbenzene/lb styrene (32 g ethylbenzene/kg styrene).⁹ This corresponds to 9.6×10^{-6} lb benzene/lb styrene (9.6×10^{-3} g benzene/kg styrene). Benzene in shipping and storage (Vent F in Figure 5-1) must also be considered as a source if benzene is not produced on site (in which case these emissions would be considered part of the benzene production process).

Benzene Emissions from Styrene Production Using Ethylbenzene Hydroperoxidation

Only one U.S. facility currently reports using this method. Emission estimates presented in this section are based on a capacity of 1200 million lb styrene/yr (544 million kg styrene/yr).

The three main process emission sources are the ethylbenzene oxidation reactor vent (A in Figure 5-3), the propylene recycle purge vent (B), and the vacuum column vents (C) and (D). Propane vapor (B) is considered a fuel if it is not vented to the atmosphere. Of these sources, only the vacuum vents are large benzene emitters. These emissions result from benzene impurities in the ethylbenzene feed, which may result in minor side reactions in the process train.

The ethylbenzene oxidation reactor vent (A) releases CO, light organics, entrained aromatics with nitrogen, oxygen, and CO₂. The vent gas is scrubbed with oil and water for a 99 percent removal efficiency for organics. The resulting vent stream contains approximately 35 ppm benzene (0.11 mg benzene/l) or 15.9 lb benzene/hr (7.2 kilograms benzene per hour [kg/hr]).⁷⁴

The propylene recycle vent (B) releases propane, propylene, ethane, and other impurities. No flow volume data are available but, based on a similar procedure in high-grade propylene production, this stream is a high-Btu gas and would be used as a fuel. No significant benzene emissions are expected.⁷⁴

The ethylbenzene hydroperoxidation process contains numerous vacuum columns and evaporators. Vents on these operations (C-1 to C-3) release inerts and light organics dissolved in the column feeds, nitrogen used for process pressure control, and entrained aromatics. A combined vent flow is reported to be 264,200 gal/hr (1.0x10⁶ l/hr) containing about 60 lbs benzene/hr (27 kg benzene/hr).⁷⁴

The dehydrogenation vent (D in Figure 5-3) may be an emergency pressure vent similar to the separation vent (C in Figure 5-2). No specific information is available on storage, transport, or fugitive emissions for this process.

5.1.6 Control Technology for Ethylbenzene/Styrene Processes

Control methods for the two ethylbenzene/styrene processes in use in the United States include condensation, adsorption, flaring, and combustion in boilers or other process heaters. Controls for fugitive emissions from storage tanks, equipment leaks, and others include the use of floating-roof tanks and leak detection/correction programs. No information is available on control methods specific to the two processes mentioned in this report but not in use in the United States.

Condensers may be used to control benzene emissions associated with ethylbenzene/styrene production. The control efficiency of a condenser is determined by the temperature and pressure at which the condenser operates and by the concentration and vapor pressure of the organics in the vent stream. At typical pressures of 1 to 3 atmospheres and coil temperatures of 36 to 41 °F (2 to 5 °C), condensers can achieve 80 to 90 percent benzene reduction when used on vent streams at 70 to 100 percent saturation in benzene at 104 to 122 °F (40 to 50 °C).⁷⁴ Higher efficiencies become prohibitively expensive.

Condensers have limited use in handling high-volume streams, short duration emergency releases, or cyclic releases such as from the hydrogen separation vent. Furthermore, condensers are inefficient at low saturations such as with the alkylation reactor vents and the column vents of Figure 5-1.

In an ethylbenzene/styrene plant, a packed tower can be used to remove benzene. PEB and various ethylbenzene produced during benzene alkylation are good absorbers of benzene and are normally recycled. This system is unsuitable, however, for handling high-volume or intermittent releases of gases beyond the tower design capabilities.

Absorption systems can maintain 80 to 99 percent benzene removal efficiencies for both saturated and unsaturated benzene streams, depending on the tower design and operating variables.

Flare systems can control some streams for which condensation or absorption is not suitable. Flares can efficiently handle highly saturated streams such as from the alkylation vents. They can also control upset releases and other irregular releases, although efficiency can be variable. The major difficulty here occurs in manifolding. High-nitrogen or other low- or non-combustible gases may also be problematic. Consequently, there are no conclusive data on flare efficiency. Limited data show benzene destruction efficiencies ranging from 60 to 99 percent. A properly designed flare system must account for a range of flow and gas composition as well as the potential for explosion.

Use of vent gases as a fuel combined with regular process fuel is advantageous because vent flow variations can be better accounted for. Also, better gas/air mixing occurs along the entire flare front. As with flares, however, manifolding to ensure optimal combustion characteristics is the major technical problem. Process pressure variations and the possibility of emergency releases are complicating factors.

5.2 CYCLOHEXANE PRODUCTION

About 15 percent of the U.S. supply of benzene is used to produce cyclohexane.¹⁰ Table 5-3 lists the location and current capacity for U.S. cyclohexane producers.¹¹ Two basic methods are used to produce cyclohexane: hydrogenation of benzene and petroleum liquid separation. Most of the cyclohexane produced domestically is produced through hydrogenation of benzene. The following discussions of these two processes are taken from Reference 76.

TABLE 5-3. U.S. PRODUCERS OF CYCLOHEXANE

Company	Location	Annual Capacity millions of gal (l)
Chevron Chemical Company	Port Arthur, TX	38 (144)
Phillips Petroleum Company		
Specialty Chemicals Branch	Borger, TX	35 (132)
Olefins and Cyclics Branch	Sweeny, TX	90 (341)
Phillips Puerto Rico Core, Inc.	Guayama, PR	100 (379)
Texaco Chemical Company	Port Arthur, TX	75 (284)
CITGO Petroleum Corporation	Corpus Christi, TX	30 (114)
TOTAL		368 (1,393)

Source: Reference 11.

Note: This list is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current lists and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel. These plant locations and capacities were current as of January 1, 1993.

5.2.1 Process Description for Cyclohexane Production via Benzene Hydrogenation

Figure 5-5 shows a model flow diagram for the manufacture of cyclohexane by benzene hydrogenation.⁷⁶ High-purity benzene (Stream 1) is fed to the catalytic reactors in parallel and hydrogen (Stream 2) is fed into the reactors in series. Part of the cyclohexane separated in the flash separator is recycled (Stream 3) and fed to the reactors in series. Recycling helps to control the reactor temperature, because the reaction is highly exothermic. The temperature is also controlled by generating steam, which is used elsewhere in the petrochemical complex. Both platinum and nickel catalysts are used presently to produce cyclohexane.

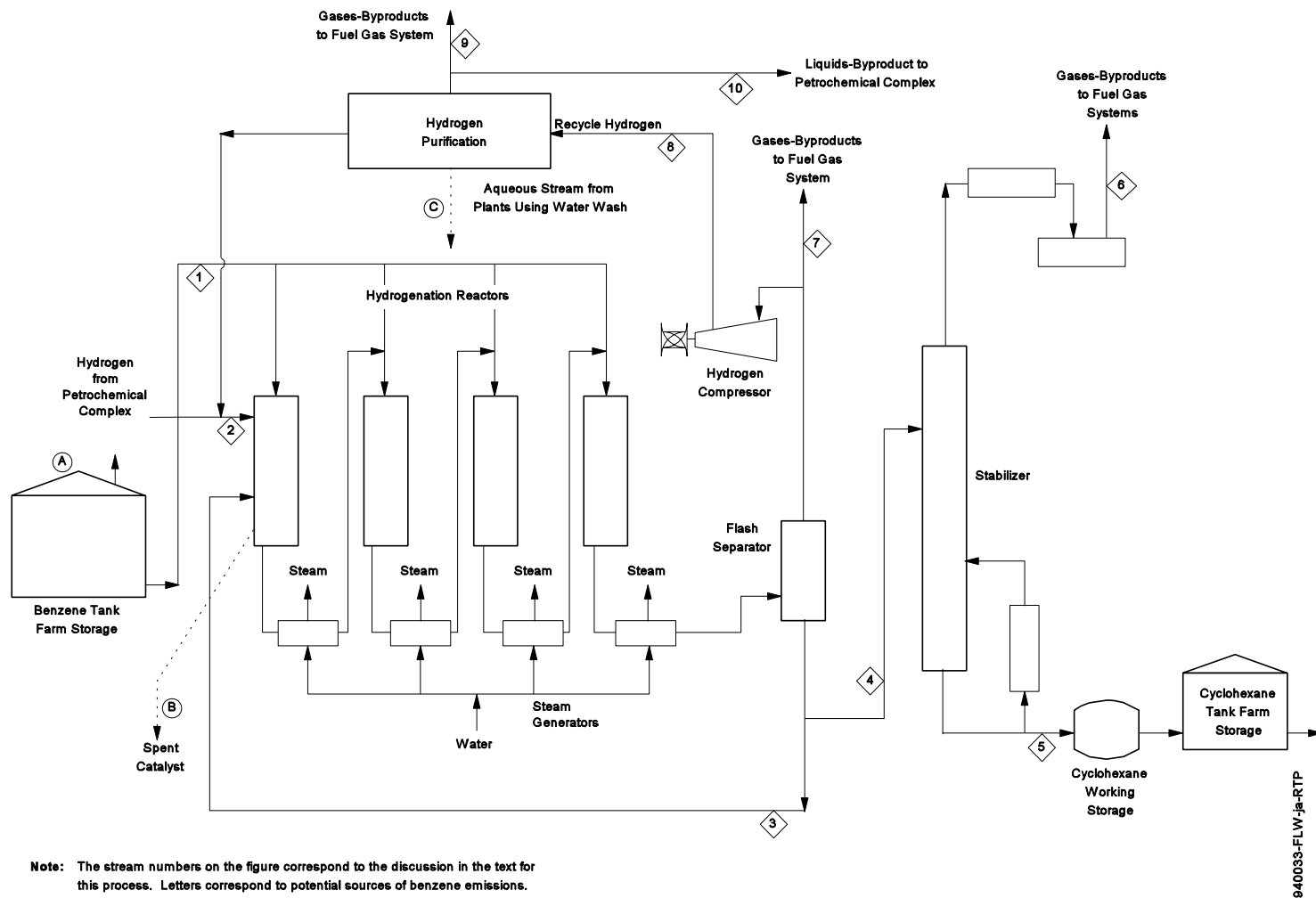


Figure 5-5. Process Flow Diagram for Cyclohexane Production Using the Benzene Hydrogenation Process

Source: Reference 76.

After leaving the flash separator, the cyclohexane (Stream 4) is sent to a distillation column (stabilizer) for removal of methane, ethane, other light hydrocarbons, and soluble hydrogen gas from the cyclohexane product. These impurities (Stream 6) are routed to the fuel-gas storage system for the facility and used as fuel in process heaters. Cyclohexane (Stream 5) purified in the stabilizer may be greater than 99.9 percent pure. The residual benzene content is typically less than 0.0042 lb/gal (500 mg/l). This pure product is stored in large tanks prior to shipment.

Gas from the flash separator, largely hydrogen, is not pure enough for direct reuse. Therefore, the stream (8) is purified before being recycled to (Stream 2) the reactor. Typical processes used for hydrogen purification are absorption and stripping of the hydrogen gas and cryogenic separation. Some plants use a combination of the two processes. Organic liquids (Stream 10) that are separated from the hydrogen in the hydrogen purification unit are sent to other petroleum processing units in the petrochemical complex. The separated gases (Stream 9) are used as fuel gas.

Depending on the type of hydrogen purification used, inert impurities present in the gas from the flash separator can be purged from the system before the gas enters the hydrogen purification equipment. This stream (7) is sent to the fuel gas system.

5.2.2 Benzene Emissions from Cyclohexane Production via Benzene Hydrogenation

There are no process emissions during normal operation.⁷⁶ During shutdowns, individual equipment vents are opened as required during final depressurization of equipment. Except for the feed streams, the concentration of benzene in the process equipment is low; therefore, few or no benzene emissions would be expected during a shutdown.⁷⁶

Equipment leak emissions from process pumps, valves, and compressors may contain benzene or other hydrocarbons. Storage of benzene (Vent A in Figure 5-5) may also contribute to benzene emissions.

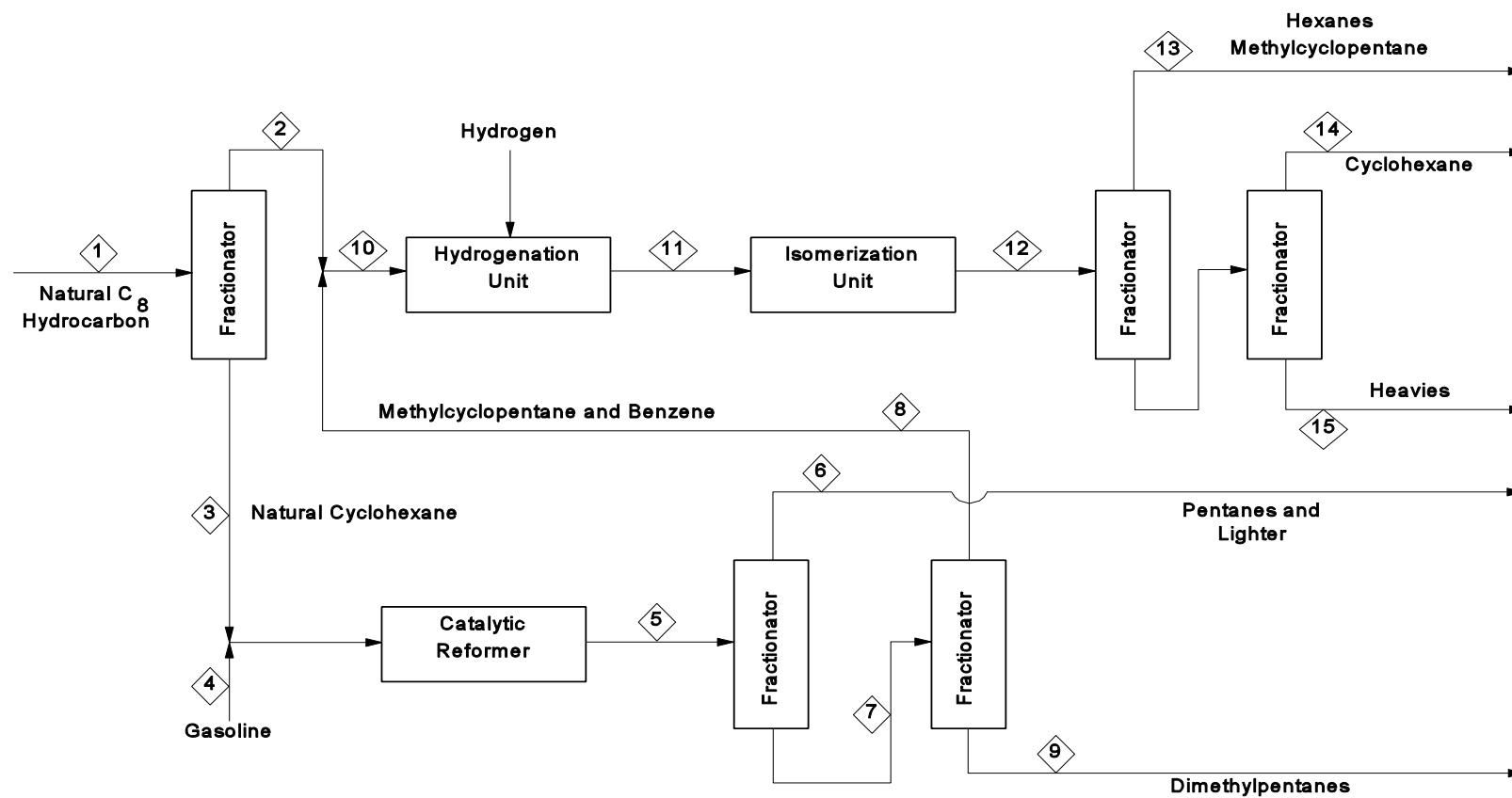
Other potential sources of emissions are catalyst handling (B) and absorber wastewater (C) (when an aqueous solution is used to purify the recycled hydrogen). Caution is taken to remove the organic compounds from the spent catalyst before it is replaced. The spent catalyst is sold for metal recovery.⁷⁶

5.2.3 Process Description for Cyclohexane Production via Separation of Petroleum Fractions

Cyclohexane may also be produced by separation of select petroleum fractions. The process used to recover cyclohexane in this manner is shown in Figure 5-6.⁷⁶ A petroleum fraction rich in cyclohexane (Stream 1) is fed to a distillation column, in which benzene and methylcyclopentane are removed (Stream 2) and routed to a hydrogenation unit. The bottoms (Stream 3) from the column containing cyclohexane and other hydrocarbons are combined with another petroleum stream (4) and sent to a catalytic reformer, where the cyclohexane is converted to benzene. The hydrogen generated in this step may be used in the hydrogenation step or used elsewhere in the petrochemical complex.

The benzene-rich stream (5) leaving the catalytic reformer is sent to a distillation column, where compounds that have vapor pressure higher than benzene (pentanes, etc.) are removed (Stream 6) and used as byproducts. The benzene-rich stream (7) that is left is sent to another distillation column, where the benzene and methylcyclopentane (Stream 8) are removed. The remaining hydrocarbons (largely dimethylpentanes) are used elsewhere in the petrochemical complex as byproducts (Stream 9).

Stream 8 (benzene and methylcyclopentane) is combined with Stream 2 and sent to a hydrogenation unit (Stream 10). Hydrogen is fed to this unit and the benzene is converted to cyclohexane. Isomers of cyclohexane, such as methylcyclopentane, are converted to cyclohexane in an isomerization unit (Stream 11) and the effluent from this equipment (Stream 12) is separated in a final distillation step. Pure cyclohexane (Stream 14) is separated from isomers of cyclohexane (Stream 13) and compounds with lower vapor pressures (Stream 15).



Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 5-6. Process Flow Diagram for Cyclohexane from Petroleum Fractions

Source: Reference 76.

5.2.4 Benzene Emissions from Cyclohexane Production via Separation of Petroleum Fractions

There are no process emissions during normal operation.⁷⁶ During emergency shutdowns, individual equipment vents are opened as required.

Equipment leaks can be sources of benzene, cyclohexane, methane, or other petroleum compound emissions. Leaks from heat exchangers into cooling water or steam production can be a potential fugitive loss. Equipment leak losses have special significance because of the high diffusivity of hydrogen at elevated temperatures and pressures and the extremely flammable nature of the liquid and gas processing streams.⁷⁷ No specific emission factors or component counts (valves, flanges, etc.) were found for benzene associated with equipment leak emissions at these plants.

A potential source of benzene emissions is catalyst handling. Special efforts are made to remove the organic compounds from the spent catalyst before it is replaced. The spent catalyst is sold for metal recovery.⁷⁶ No emission factors were found for benzene as related to catalyst handling.

5.3 CUMENE PRODUCTION

In the United States, all commercial cumene is produced by the reaction of benzene with propylene. Typically, the catalyst is phosphoric acid, but sulfuric acid or aluminum chloride may be used. Additionally, various new processes based on solid zeolite catalysts were introduced during 1993; however, information about these new processes is limited, and they are not discussed in this section. The location and capacities of U.S. producers of cumene are provided in Table 5-4.^{11,78}

TABLE 5-4. U.S. PRODUCERS OF CUMENE

Plant	Location	Annual Capacity million lb (million kg)	Notes
Ashland Chemical Company	Catlettsburg, KY	550 (249)	Cumene is sold
BTL Specialty Resins Corporation	Blue Island, IL	120 (54)	Captive for phenol and acetone
Chevron Chemical Company	Philadelphia, PA	450 (204)	Cumene is sold
	Port Arthur, TX	450 (204)	Cumene is sold
Citgo Petroleum Corp. (Champlin)	Corpus Christi, TX	825 (374)	--
Coastal Refining	Westville, NJ	150 (68)	Cumene is sold
Georgia Gulf Corporation	Pasadena, TX	1,420 (644)	Some cumene transferred to company's phenol/acetone plant
Koch Refining Company	Corpus Christi, TX	750 (340)	Cumene is sold
Shell Chemical Company	Deer Park, TX	900 (408)	Captive for phenol/acetone
Texaco Chemical Company	El Dorado, KS	135 (61)	Captive for phenol/acetone

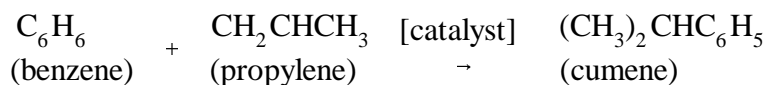
Source: References 11 and 78.

Note: This list is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current list and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel. These locations, producers, and capacities were current as of November 1993.

5.3.1 Process Descriptions for Cumene Production by Alkylating Benzene with Propylene

Cumene is present in crude oils and refinery streams. However, all commercial cumene is produced by the reaction of benzene and propylene.

Benzene and propylene are reacted at elevated temperatures and pressures in the presence of an acidic catalyst. A simplified equation for this reaction is as follows:



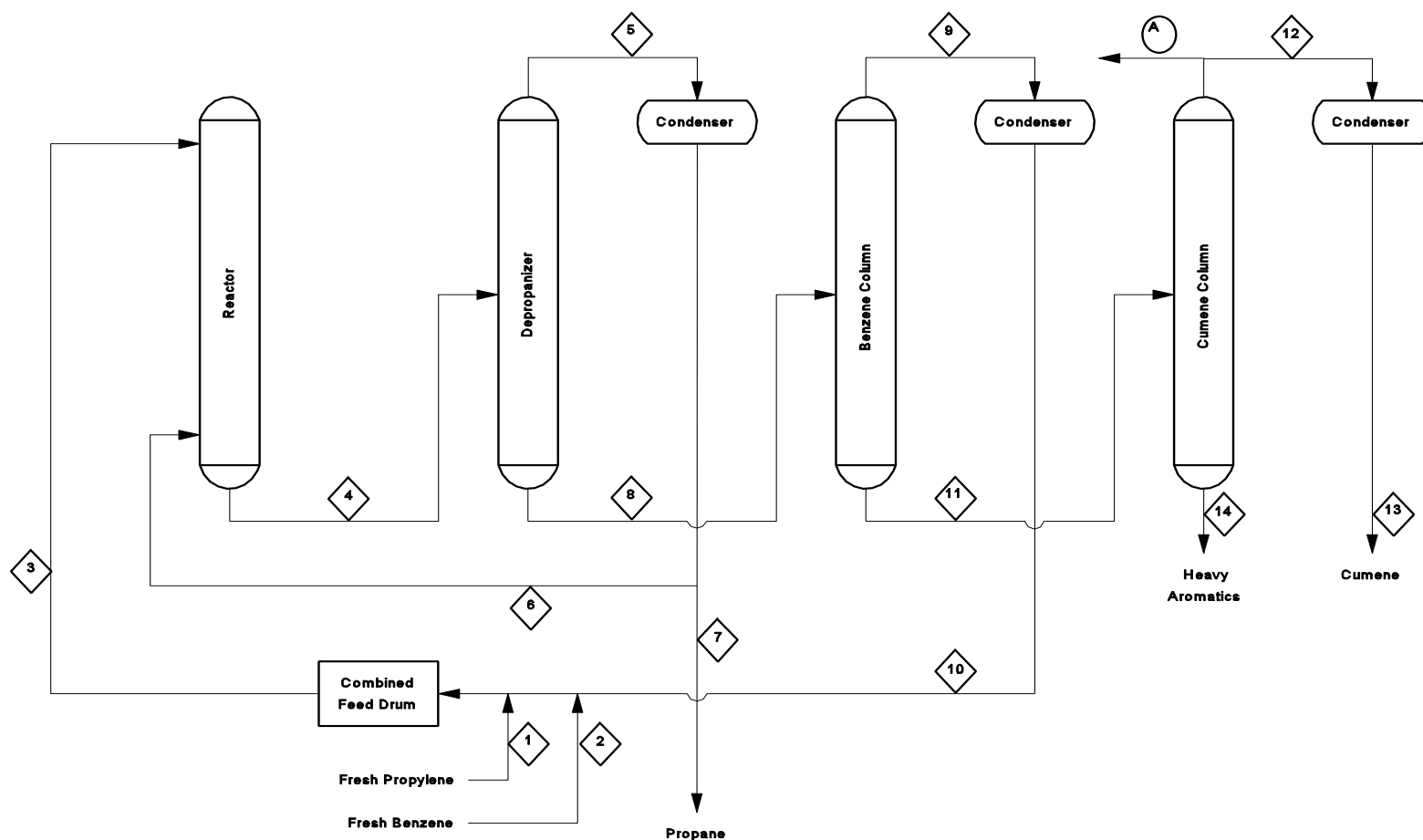
The exothermic reaction is typically conducted using solid phosphoric acid as a catalyst, but the reaction may also be conducted using aluminum chloride or sulfuric acid as the catalyst. The aluminum chloride and sulfuric acid processes are similar; therefore, the sulfuric acid process is not described here.⁷⁹

Solid Phosphoric Acid Catalyst Process

Figure 5-7 is a typical flow diagram for the manufacture of cumene by the process using phosphoric acid as the catalyst support.⁸⁰ Solid phosphoric acid is the most favored catalyst system for manufacturing cumene and is a selective alkylation catalyst that promotes the alkylation of benzene with propylene in a vapor-phase system.⁷⁹

Because the catalyst is selective, propylene feedstock for this process does not have to be thoroughly refined before use. Crude propylene streams (Stream 1) from refinery crackers that are fractionated to about 70 percent propylene can be used without further purification. The benzene (Stream 2) used in this process does not have to be dried before use because the catalyst system requires small amounts of water vapor in the reactor stream to activate the catalyst.⁷⁹

Propylene and benzene (Streams 1 and 2) are combined in a feed drum and then fed (Stream 3) to a reactor containing the phosphoric acid catalyst. The feed ratio is normally at least four moles of benzene per mole of propylene. An excess of benzene is maintained in order to inhibit side reactions. The propylene is completely consumed. From the reactor, the byproducts, unreacted material, and product are separated by distillation. The reaction products (Stream 4) are sent to a depropanizers where residual hydrocarbons (mostly propane) are removed. The propane (Stream 5) is sent through a condenser, after which some of the



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Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 5-7. Process for the Manufacture of Cumene Using Solid Phosphoric Acid Catalyst

Source: Reference 80.